

# Protection from soil erosion through calcium phosphate precipitation

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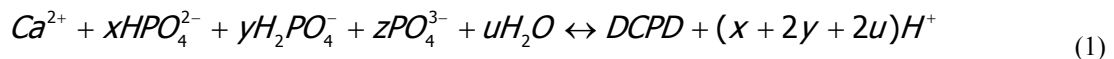
## 1. Abstract

An environmentally friendly method to protect surface soil from erosion has been developed. The method involves in situ precipitation of calcium phosphate through the development of the appropriate supersaturation conditions. The growing, sparingly soluble crystallites form a network entangling loose soil grains. The method we present aimed at meeting the challenge of the enhancement of the soil strength against strains of raindrops. The mineral deposition should be carried out in a way that sufficient infiltration of water and aeration of soil are maintained. The anticipated gradual dissolution of the deposited phosphate salt with time is expected to fertilize soil, enriching it with P, Ca and K ions, important nutrients for plant growth. The conditions of forming calcium dicalcium phosphate dihydrate (DCPD) on soil grains are presented. The precipitation of DCPD in the presence of soil was investigated in a batch stirred reactor mixing  $\text{KH}_2\text{PO}_4$  and  $\text{CaCl}_2$  solutions. The exact concentration range was determined through a series of preliminary experiments. In all cases the conditions selected resulted in the spontaneous precipitation of DCPD. The batch reactor parametric investigation was followed by direct visual observations of crystal growth within a glass micromodel in order to specify whether nucleation of DCPD crystals was initiated on the soil grains selectively. The information obtained was applied in an indoor test land plot, having a total surface area of  $1\text{m}^2$ , filled with crusted and sieved top soil from a Greek agricultural region (43% sand, 46% silt, 11% clay). The solutions were sprayed on the soil which was next left to attain its natural moisture. The method was tested under simulated rainfall. The runoff and infiltration rates were measured. The precipitation of DCPD in situ resulted, for a test time period of 30 minutes, in the reduction of runoff rate by 20% and in the enhancement of infiltration in the experimental conditions tested. These results are very promising and further research is in progress.

## 2. Introduction

Surface runoff and erosion are responsible for low productivity rates and soil is mostly susceptible to these processes during the period before the plant growth. Poor structure and weak aggregate stability are properties which make soils prone to erosion [Singer (1991)]. The method presented in this paper aimed at reducing soil deterioration due to grains detachment caused by the fall of raindrops. More specifically, calcium phosphate, a sparingly soluble salt may be precipitated *in situ*, through the development of the appropriate local supersaturation conditions. The salt which precipitates and outgrows, results in binding together the loose soil grains. The new soil-salt composite structure obtained may be managed through the appropriate precipitation conditions, so that adequate water infiltration and soil aeration are maintained. The anticipated gradual dissolution of the deposited phosphate salt with time is expected to fertilize soil, enriching it with P, Ca and K ions which are important nutrients for the growth of plants. Furthermore, clay swelling, which plays a crucial role in soil sealing, is expected to decrease with increasing electrolyte concentration [Qadir et al. (2002)].

In the present work we have focused on the formation of dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , DCPD) the acid phase of the calcium phosphate system, which may be precipitated from the respective supersaturated solutions according to the reaction:



For each mole of  $\text{Ca}^{2+}$  or  $\text{H}_2\text{PO}_4^-$  removed from solution, one mole of DCPD forms with the release of equivalent amounts of  $\text{H}^+$  ions according to the stoichiometry of (1). The supersaturation ratio,  $\Omega$ , with respect to DCPD, is defined as:

$$\Omega = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HPO}_4^{2-}}}{K_s^0} \quad (2)$$

where  $K_s^0$  is the thermodynamic solubility product of DCPD.

Observations in glass micromodels have been extensively utilized to study multiphase flow phenomena in porous media [Lenormand et al. (1983), Kanellopoulou et al. (2007)]. In order to specify if precipitation of DCPD crystals is initiated on the soil grains, a series of optical observation experiments were conducted in the presence of soil sludge. Finally, scaling up and evaluation of the proposed method was done by soil erosion tests using simulated rainfall. The duration of each application was 30 min because the product of kinetic energy and 30-minute intensity was found to be the best single rainfall parameter for predicting soil loss [Wischmeier et al. (1958)] while the steepness of soil surface was of 20 degrees.

### 3. Methods

#### *Soil sampling and sludge preparation*

Top soil (0-20 cm depth) from a Greek agricultural field was collected, dried in air, sieved through a 2 mm diameter sieve and was characterized according to Gee et al. (1986). The mechanical analysis showed a composition of 43% silicate sand, 11% clay and 46% silt. The most common elements present in the soil used in our experiments were Si, Ca, Al, Fe, Mg, K and C from the organic compounds and the total carbon amount was measured equal to 39.5 mg·g<sup>-1</sup> soil. The Mg<sup>2+</sup> and Ca<sup>2+</sup> concentrations in the aqueous phase, past equilibration of 1:5 soil - water mixtures were 0.15 and 0.09 mmol·l<sup>-1</sup> respectively. The nitrogen B.E.T. specific surface area of the soil was found equal to 3.1 m<sup>2</sup>·g<sup>-1</sup>, while in a 1:1 (w/w) slurry of soil: water and 1:2 (w/w) slurry of soil: CaCl<sub>2</sub> 0.02 mol·l<sup>-1</sup>, the conductivity and the pH of the soil used were 420 μS·cm<sup>-1</sup> and 6.8-7.4, respectively. Sludge of this soil used in the experiments was made mixing dry soil grains of diameter <2 mm with a 0.1 mol·l<sup>-1</sup> KCl solution to a final concentration of 1 g·ml<sup>-1</sup>, for 24 hr. Next, it was stored into a dialysis cellulose tubing and was dialyzed against a KCl 0.1 mol·l<sup>-1</sup> solution in order to remove low molecular weight impurities. The density of the sludge was 1.4±0.1 g·ml<sup>-1</sup>.

#### *Visualization of calcium phosphate growth*

Visualization experiments were conducted in pore-scale etched networks, produced by etching a network pattern of grains on a glass plate. Soil sludge aggregates were introduced in the simulation glass networks. The calcium phosphate supersaturated solutions were prepared by injecting two solutions from parallel syringes; one solution containing twice the concentration of the required calcium ions and the other twice the phosphate content. The solutions were mixed in a plastic tube 5 cm in length and 0.5 mm in diameter, prior to the injection point of the porous network, thus ensuring good mixing. The depth of the channels was about 0.3 mm. The precipitation of calcium phosphate was monitored by a microscope (ZEISS), connected to a video camera (AXIS 223M Network Camera) and a PC equipped with the corresponding imaging software (AXIS Camera Station). The pore network was filled with 0.1M KCl as background electrolyte followed by the injection of 0.2 g of the soil sludge. The experiments started with the initiation of pumping the supersaturated calcium phosphate solutions. All experiments were conducted at room temperature (25°C) and the flow rate was 5 ml/hr.

#### *Rainfall simulator*

Experiments were carried out in a rainfall simulator which was constructed for this purpose. The rainfall was generated by a Fulljet nozzle (Spraying Systems) installed 2.5 m above the test plot. The rainfall coverage was of 1.2 m radius, the Christiansen coefficient was found to be 73.5% and the distribution of drop size was given by the company's technical report equal to D<sub>50</sub>=2.5 mm.

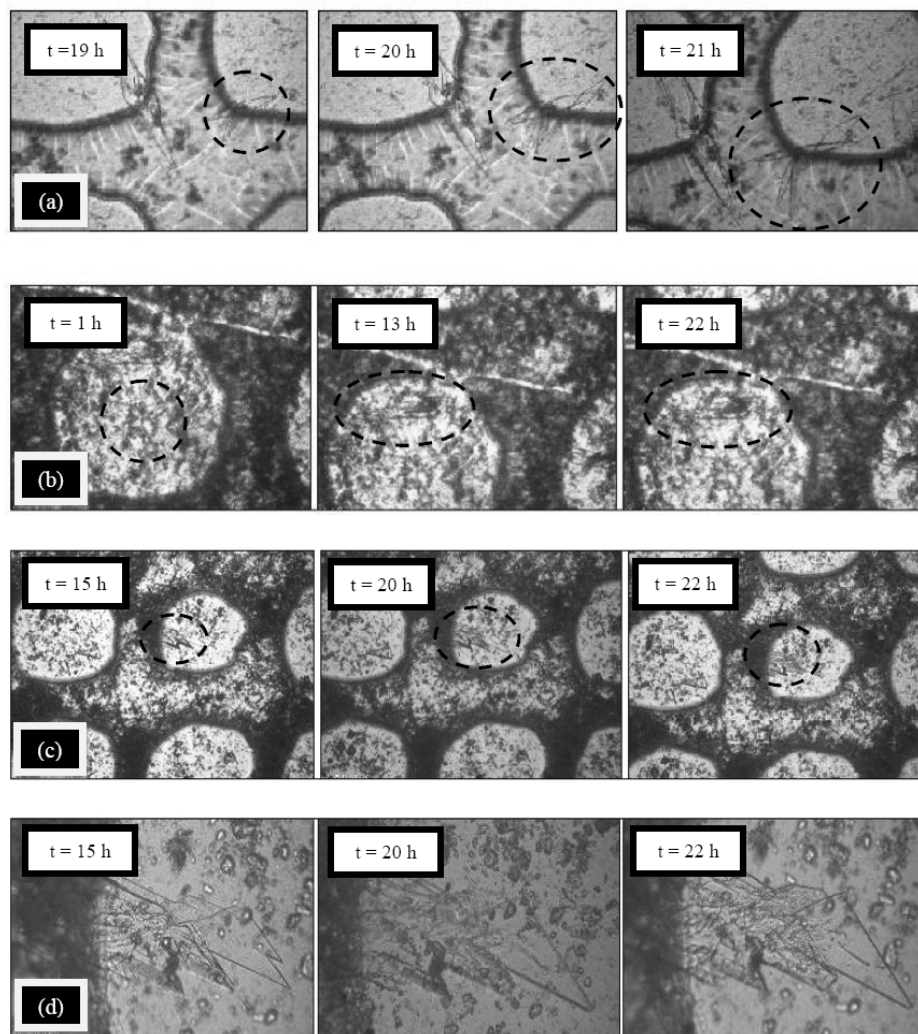
Soil was air-dried, crusted and sieved through a 2 mm diameter sieve. It was uniformly packed in a tray of total area 1m<sup>2</sup>, held by a very thin mesh, which allowed water to infiltrate naturally. Under the mesh, the space was adequate so that there was no change in soil's moisture and at the bottom there were holes to collect the percolated water. Before any rainfall application the soil surface was smoothened. Soil treated with the supersaturated solutions with respect to DCPD was left to obtain its natural moisture and then was exposed in artificial rain for 30 min with rain intensity of I=40 mm/h ("ten year return period"). Soil samples were collected in order to verify the formation of the calcium phosphate phase.

### 4. Results

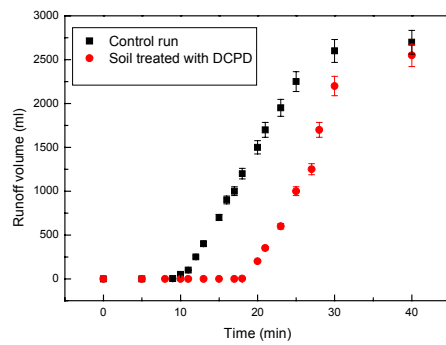
The experiments done for the visualization of DCPD growth were conducted at supersaturation values of  $\Omega=15$  and  $\Omega=20$  at 25°C, with different amounts of sludge introduced in the porous medium. As may be seen in Figure 1, DCPD appeared as transparent precipitated crystals with sizes up to 2 mm. As expected according to

the kinetic results obtained from batch experiments, the rates of precipitation were higher at higher supersaturation rates and crystal growth was completed faster. At  $\Omega=20$  the reaction was faster when more sludge was added in the porous medium (Figure 1(b)) than the corresponding case (a), where less sludge was added. This phenomenon could be attributed due the amount of heterogeneities introduced in the system, which accelerate heterogeneous crystal growth and precipitation. The crystals did not show any preference to grow either on the etched glass patterns of the porous medium or in the void space among them. On the contrary, almost in all cases DCPD crystals appear to prefer precipitating on soil sludge particles.

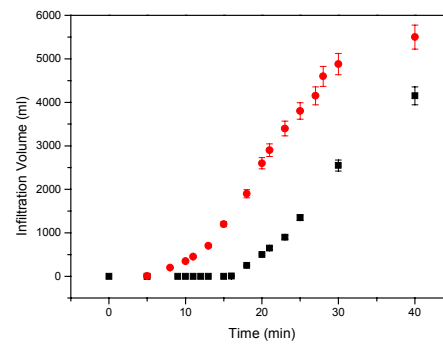
The application of the supersaturated solutions with respect to DCPD changed the hydraulics of the soil bed significantly. At bare soil run, rainwater leaves soil bed mainly because of runoff process, which was predominant and its rate was found to be equal to 154.54 ml/min; this is why percolation rate became measurable only past the lapse of 18 min. In the case of the treatment run under the same rainfall characteristics, infiltration was enhanced from the beginning of the rainfall precipitation while runoff was delayed as may be seen in Figure 2 while the respective rate was lower and equal to 123.36 ml/min. In Figure 3 images of bare soil and soil with DCPD treatment are presented. It may be seen that microrills in the second case are not so intense, deep and long, which is in agreement with the lower runoff rate and stands as a good indicator for lower soil loss. These results suggest that applications of calcium phosphate dihydrate precipitation in soil consolidation are promising.



**Figure 1** Images of DCPD crystals, precipitated in porous media in the presence of sludge. (a)  $\Omega=20$ ,  $25^{\circ}\text{C}$ ; (b) as in (a) with more soil sludge; (c)  $\Omega=15$ ,  $25^{\circ}\text{C}$ ; (d) magnification of (c). DCPD crystals are noted with dashed lines



(a)



(b)

Figure 2 Graphs of (a) Runoff rate; (b) Infiltration rate



(a)



(b)

Figure 3 Images of (a) bare soil and (b) soil treated with DCPD supersaturated solution  $\Omega=20$ , after 30 min exposure to 40mm/hr rainfall

## 5. References

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## 6. Acknowledgements

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